

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 September 2001 (13.09.2001)

PCT

(10) International Publication Number
WO 01/66633 A1

(51) International Patent Classification⁷: C08K 5/35, (74) Agent: MOOIJ, Johannes, Jacobus; DSM Patents & C08G 69/48, 69/20, 63/91 Trademarks, P.O. Box 9, NL-6160 MA Geleen (NL).

(21) International Application Number: PCT/NL01/00199

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(22) International Filing Date: 9 March 2001 (09.03.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1014604 10 March 2000 (10.03.2000) NL

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): LOONTJENS, Jacobus, Antonius [NL/NL]; Synagogeplantsoen 76, NL-6231 KK Meerssen (NL). PLUM, Bartholomeus, Johannes, Margretha [NL/NL]; Klein Bergemmerweg 52, NL-6235 AJ Ulestraten (NL).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/66633 A1

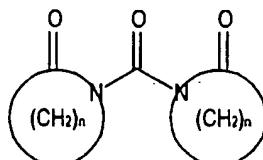
(54) Title: CHAIN EXTENSION PROCESS

(57) Abstract: The invention relates to a process for preparing a high-molecular polymer by contacting in a melt a difunctional lowermolecular polymer whose functional end groups are -OH or -NH₂ groups with carbonylbislactamate, characterized in that the melt also contains an acid or a base as a catalyst. If the difunctional polymer contains a -COOH group, it is preferred for the melt also to contain a bisoxazine or a bisoxazoline.

5

CHAIN EXTENSION PROCESS

The invention relates to a process for preparing a high-molecular weight polymer by contacting in a melt a difunctional polymer having a lower molecular weight whose end functional groups are $-\text{OH}$ or $-\text{NH}_2$ groups with 10 a carbonylbislactamate (CBL) with the following formula:



wherein n is an integer from 3 to 15. Preferably the carbonylbislactamate is 15 carbonylbiscaprolactamate (CBC), with n = 5.

A similar process is disclosed in WO 98/47940. WO 98/47940 describes a process for preparing a high-molecular weight polyamide by contacting polyamide having a lower molecular weight in the melt with carbonylbiscaprolactamate (CBC).

20 A drawback of that process is that the reaction proceeds comparatively slowly.

The object of the invention is to provide a process that does not have the aforementioned drawback or has the aforementioned drawback to a lesser extent.

25 This object is achieved by the melt also containing an acid or a base. The acid or base has the function of a catalyst.

This ensures that the reaction proceeds more rapidly, as is apparent from the fact that the viscosity increases much more rapidly with catalyst than without catalyst. This can be established from for example the increase in the 30 torque of a Brabender in which a blend of a difunctional polymer and CBL is kneaded optionally in the presence of an acid or a base.

Acids that are suitable for use as a catalyst for chain extension in the presence of CBL are LiX , Sb_2O_3 , GeO_2 and As_2O_3 , BX_3 , MgX_2 , BiX_3 , SnX_4 , SbX_5 , FeX_3 , GeX_4 , GaX_3 , HgX_2 , ZnX_2 , AlX_3 , TiX_4 , MnX_2 , ZrX_4 , R_4NX , R_4PX , HX ,

where X = I, Br, Cl, F, OR and R = alkyl or aryl. Brønstedt acids such as H_2SO_4 , HNO_3 , HX, H_3PO_4 , H_3PO_3 , RH_2PO_2 , RH_2PO_3 , $R[(CO)OH]_n$, with n = 1-6 are also suitable.

Bases that are suitable for use as a catalyst for chain extension

- 5 in the presence of CBC are Li-versetate, Zn acetylacetone (acac), $M(OH)_n$, $(RO)_nM$ (M = alkali or earth alkali, R = alkyl with $C_1 - C_{20}$ or aryl), $NR_nH_{4-n}OH$ (R = alkyl with $C_1 - C_{20}$ or aryl), triamines such as triethylamine, tributylamine, trihexylamine, trioctylamine and cyclic amines such as diazobicyclo[2.2.2]octane (DABCO), dimethylaminopyridine (DMAP), guanidine, morfoline, dibutyl tin
- 10 dilaurate (DBTDL), dibutyl tin bis(2-ethylhexanoate), dibutyl tin dibutylate, dibutyl tin dimethylate, dibutyl tin dioctanoate.

It is preferred for the catalyst to be a Lewis acid or a Lewis base.

This ensures that the time needed for curing is even shorter.

It is preferred for the Lewis acid or base to be

- 15 tetraalkoxytitanate, $Zr(OR)_4$, Li versetate, ZnAcAc in which the alkoxy group is for example a butoxy group or an isopropoxy group.

- 20 The amount of carbonylbiscaprolactamate used in the process of the invention may vary between wide limits. As a rule, at least about 0.1% by weight relative to the functional polymer is needed in order to have an appreciable effect. Amounts in excess of 3% by weight do not normally result in any further increase in molecular weight.

One skilled in the art will generally adjust the amount of carbonylbiscaprolactamate to suit the number of available functional groups and the viscosity increase that needs to result from the increased molecular weight.

- 25 He/she will normally determine the most optimum amount for his/her situation through simple experiment.

A difunctional polymer here and hereinafter means a polymer with two functional groups per molecule consisting of an -OH group or an -NH₂ group.

- 30 Examples of such polymers are polyamides, polyesters, polycarbonates and polyetherpolyols.

The process of the invention can in principle be applied for all types of polyamide. These include at least the aliphatic polyamides, for example polyamide-4, polyamide-6, polyamide-8, polyamide-4,6, polyamide-6,6,

polyamide-6,10, polyamides derived from an aliphatic diamine and an aromatic dicarboxylic acid, for example polyamide-4,T, polyamide-6,T, polyamide-4,I, where T stands for terephthalate and I for isophthalate, copolyamides of linear polyamides and copolyamides of an aliphatic and a partially aromatic polyamide, 5 for example polyamide 6/6,T and 6/6,I.

Suitable polyesters for which the process of the invention may be applied are at least polyesters derived from aliphatic dicarboxylic acids and diols, polyesters of aliphatic and cycloaliphatic diols and aromatic dicarboxylic acids, copolymers that are partly aliphatic and partly aromatic and polyesters 10 which contain units that are derived from cycloaliphatic dicarboxylic acids.

Examples hereof are polybutylene adipate, polymethylene terephthalate, polyethylene terephthalate, polyethylene naphthalate, polybutylene terephthalate, copolymers of polybutylene adipate and polybutylene terephthalate and the polyesters derived from butane diol and cyclohexanedicarboxylic acid

15 The polyetherpolyols, for which the process of the invention may be applied are polyols, which possess a oxyalkylene structure, composed of a oxyalkylene group, with 1-10 carbon atoms an oxygen atom as repeating unit and which preferably are a diol. Examples of polyetherpolyols are polyoxymethylene, polyethylene glycol, polypropylene glycol, polytetramethylene glycol,

20 polyheptamethylene glycol, polyhexamethylene glycol and polydecamethylene glycol.

The process of the invention can readily be carried out using the customary techniques and melt blending equipment, for example by blending the lower molecular polyamide and the carbonylbis(lactam) and optionally other 25 additives in the solid phase, for example in a tumble dryer, whereupon the obtained blend is melted in a customary melt blender, for example a Haake kneader, a Brabender blender or a twin-screw or double-screw extruder. The various components may also be added to the blending equipment separately.

The carbonylbis(lactam) and catalyst may also be added to a 30 polymer product stream of a functional polymer having a lower molecular weight as it exits from a polymerization reactor in which this polymer was polymerized.

The polymerization process may be operated batch-wise or continuously. In the former case, the residence time in the reactor can be shortened and so productivity can be increased and the postcondensation step 35 can be omitted.

In the process of the invention, CBL reacts solely with the $-\text{NH}_2$ groups or the $-\text{OH}$ functional groups of the functional polymers. Functional polymers that also possess $-\text{COOH}$ functionality react with either the $-\text{OH}$ functional groups or the $-\text{NH}_2$ functional groups. If $-\text{COOH}$ functionality is present

5 in the melt, it is preferred not only for CBL and the catalyst but also a bisoxazine or a bisoxazoline to be present in the process of the invention. This ensures that the reaction proceeds even more rapidly.

It is preferred for the bisoxazoline to be 1,4-phenylenebisoxazoline.

10 The invention will be elucidated on the bases of the following examples.

Example 1

CBC is added to grinded and dried PET with 2 $-\text{OH}$ end groups

15 and a relative viscosity of $\eta = 1,59$ in a molair ratio of 1:2 (CBC:PET). 1 wt% of catalyst with respect to the amount of CBC was added. All the PET samples were extruded in a laboratory extruder for 15 gram samples at 280° with a residence time of 4 minutes. The resulting viscosities are given in table 1.

Table 1

Acid/Base	Relative viscosity
Para toluene sulfonic acid	1.77
MgBr ₂	1.77
NaOC ₂ H ₅	1.78
DBTDL	1.79
SnCl ₄	1.81
VO(iOPr) ₃	1.81
DABCO	1.83
LiOCH ₃	1.83
LiBr	1.83
LiI	1.83
Zn(acac) ₂	1.84
LiCl	1.87
Zr(acac) ₄	1.87
Zr(IV)(OC ₄ H ₉) ₄	1.88
Li-versetate	1.94

iOPr = isopropoxy

Comparative Experiment A

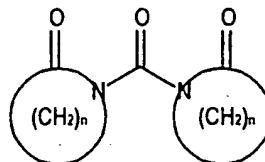
5 Example 1 was repeated without adding any catalyst. The relative viscosity increased from 1.59 to 1.76

From these experiments it can be concluded that the addition of acids and bases in a process for preparing a high-molecular weight polymer by contacting in a melt a difunctional low-molecular weight polymer with a 10 carbonylbislactamate results in a faster increase in molecular weight and thus chain extension than without an acid or a base.

It may further be concluded that preferably lithium chloride, zirconium(IV)butoxide, zirconium acetylacetone or lithium versetate are added.

CLAIMS

1. Process for preparing a high-molecular polymer by contacting in a melt a difunctional lowermolecular polymer whose end functional groups are –
5 OH or –NH₂ groups with a carbonylbislactamate with the following formula:



10 wherein n is an integer from 3 to 15, characterized in that the melt also contains an acid or a base.

2. Process according to Claim 1, in which the catalyst is a Lewis acid or a Lewis base.

3. Process according to claim 1 or claim 2, in which the carbonylbislactamate is carbonylbiscaprolactamate.

15 4. Process according to any one of Claims 1-3, in which the difunctional polymer also contains a –COOH group and in that a bisoxazine or a bisoxazoline is also present in the melt.

INTERNATIONAL SEARCH REPORT

Intern al Application No	
PCT/NL 01/00199	

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/35 C08G69/48 C08G69/20 C08G63/91

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 47940 A (DSM NV ;LOONTJENS JACOBUS ANTONIUS (NL); PLUM BARTHOLOMEUS JOHANNE) 29 October 1998 (1998-10-29) cited in the application claims 1-3 page 5, line 23 - line 24 ---	1-4
Y	US 3 862 262 A (HENDRICK ROSS MELVIN ET AL) 21 January 1975 (1975-01-21) claims 1,14,15 column 3, line 29 - line 68 column 8, line 29 - line 53 column 9, line 10 -column 10, line 19 ---	1-4
A	EP 0 556 170 A (MONSANTO CO) 18 August 1993 (1993-08-18) claims 1,4,7,10,16 ---	1 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

25 May 2001

07/06/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Hillebrand, G

INTERNATIONAL SEARCH REPORT

Intell. Application No
PCT/NL 01/00199

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 34909 A (DSM NV ;LOONTJENS JACOBUS ANTONIUS (NL); DERKS FRANCISCUS JOHANNES) 7 November 1996 (1996-11-07) claim 1 -----	1
A	EP 0 147 792 A (STAMICARBON) 10 July 1985 (1985-07-10) claims 1,3 -----	1
A	US 4 595 746 A (GABBERT JAMES D ET AL) 17 June 1986 (1986-06-17) claims 1,2 column 1, line 14 - line 25 -----	1
A	DATABASE WPI Section Ch, Week 198823 Derwent Publications Ltd., London, GB; Class A23, AN 1988-158448 XP002157844 & JP 63 099228 A (TEIJIN LTD), 30 April 1988 (1988-04-30) abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Interr. Application No

PCT/NL 01/00199

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
WO 9847940 A	29-10-1998	AU 6856698 A			13-11-1998
		CN 1252819 T			10-05-2000
		EP 1028992 A			23-08-2000
US 3862262 A	21-01-1975	AR 199246 A			14-08-1974
		AU 6662074 A			18-09-1975
		CA 1050194 A			06-03-1979
		CH 628360 A			26-02-1982
		DE 2412106 A			19-09-1974
		ES 424226 A			01-01-1977
		FR 2221478 A			11-10-1974
		GB 1472463 A			04-05-1977
		IL 44416 A			31-12-1976
		IT 1007674 B			30-10-1976
		JP 1005084 C			30-06-1980
		JP 50029553 A			25-03-1975
		JP 54040120 B			01-12-1979
		LU 69633 A			17-10-1974
		NL 7403367 A, B			17-09-1974
		SE 422582 B			15-03-1982
		SU 843759 A			30-06-1981
EP 0556170 A	18-08-1993	US 5200498 A			06-04-1993
WO 9634909 A	07-11-1996	BE 1009365 A			04-02-1997
		AU 5409196 A			21-11-1996
		DE 69603487 D			02-09-1999
		DE 69603487 T			16-03-2000
		EP 0835276 A			15-04-1998
EP 0147792 A	10-07-1985	NL 8400006 A			01-08-1985
		DE 3471311 D			23-06-1988
		JP 60158223 A			19-08-1985
		KR 8800829 B			14-05-1988
		US 4644051 A			17-02-1987
US 4595746 A	17-06-1986	AT 65520 T			15-08-1991
		AU 571763 B			21-04-1988
		AU 5126985 A			26-06-1986
		BR 8506296 A			26-08-1986
		CA 1255039 A			30-05-1989
		CS 8509340 A			14-11-1989
		DD 240211 A			22-10-1986
		DE 3583604 D			29-08-1991
		DK 581785 A			18-06-1986
		EP 0188184 A			23-07-1986
		IE 58570 B			06-10-1993
		JP 1921238 C			07-04-1995
		JP 6049756 B			29-06-1994
		JP 61143430 A			01-07-1986
		KR 9004791 B			05-07-1990
		KR 9004794 B			05-07-1990
		PT 81686 A, B			01-01-1986
JP 63099228 A	30-04-1988	JP 2507379 B			12-06-1996